

Production of potassium manganate and barium manganate from spent zinc–MnO₂ dry cells via fusion with potassium hydroxide

Renan Azevedo da Rocha ^a, Carolina Leão Quintanilha ^a, Thayná Viana Lanxin ^a, Júlio Carlos Afonso ^{a,*}, Cláudio Augusto Vianna ^b, Valdir Gante ^b, José Luiz Mantovano ^b

^a Analytical Chemistry Department, Institute of Chemistry, Federal University of Rio de Janeiro, Av. Athos da Silveira Ramos, 149, Room A509, 21941-909 Ilha do Fundão, Rio de Janeiro, Brazil

^b Departamento de Química e Materiais Nucleares, Instituto de Engenharia Nuclear, Rua Hélio de Almeida, 75, 21941-906 Rio de Janeiro, RJ, Brazil



HIGHLIGHTS

- Zn–MnO₂ dry cells as a raw material for production of potassium manganate.
- Over 70 wt% of manganese converted into potassium or barium manganate.
- No interference of zinc and other elements in the separation step.
- ZnO and K₂SO₄ as by-products of the fusion process.
- Lower generation of final wastes.

ARTICLE INFO

Article history:

Received 23 April 2014

Received in revised form

22 June 2014

Accepted 24 June 2014

Available online 7 July 2014

Keywords:

Potassium manganate

Alkaline fusion

Spent Zn–MnO₂ dry cells

Barium manganate

ABSTRACT

This work describes a route for extracting manganese and zinc from spent zinc–manganese dioxide dry cells via fusion of the electroactive components with potassium hydroxide to form potassium manganate (K₂MnO₄) and soluble zincates. The fused mass was dissolved in aqueous KOH and the insoluble matter was separated. Under the best optimal conditions, 70–78 wt% of manganese was solubilized as K₂MnO₄ whereas 30–44 wt% of zinc was solubilized as [Zn(OH)₄]²⁻ ions. Lead was the only minor component dissolved in detectable amounts. Manganese was isolated by a one-step precipitation procedure as barium manganate (BaMnO₄) or via crystallization of K₂MnO₄. Lead and excess barium were isolated as sulfate by adding K₂SO₄. Zinc was precipitated as hydroxide after neutralizing the alkaline solution with H₂SO₄. pH control is essential to avoid decomposition of manganate ions and for the sequential precipitation of leached elements. K₂SO₄ was partially recovered as by-product after partial evaporation of the neutralized solution.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Zinc–MnO₂ dry cells (Leclanché and alkaline) are a current choice for objects where small quantities of power are required [1]. These batteries are not rechargeable and usually run out rapidly [2]. Portable devices that require such electrical power source play an increasing role in modern life. The increase of the consumption of batteries causes a more intensive exploitation of mineral resources. Only the European Union are put on the market for more than 200,000 tons of portable batteries yearly but the rate of collection

of spent batteries is still modest in the European countries [3,4]. At present, most of the spent batteries are dumped in landfills or even incinerated [3,5] instead of being recycled and constitute a source of hazardous metals in the percolate collected at the bottom of the landfill [1,6–8] and even in underground waters if the landfill is not adequately protected [1,5–11]. The concentration limits of manganese in all the types of waters are considerably lower than the limits of zinc, being the former a more hazardous metal than the latter in waters [3]. Therefore, these materials are of significant environmental concern globally.

More than 1 billion spent batteries are discarded every year in Brazil [11]. In November 2008 a new directory for batteries was approved (Directory 401 from the National Brazilian Environmental Council) [12]. It is in force since July 2009 and is very close to the

* Corresponding author.

E-mail addresses: jafonson@metalmat.ufrrj.br, julio@iq.ufrj.br (J.C. Afonso).

European Directive 2006/66/EC. It states that if the amount of mercury, cadmium and lead in each battery is below 0.0005 wt%, 0.010 wt% and 0.20 wt%, respectively, this battery may be discarded in licensed municipal landfills. All Brazilian batteries do not contain significant levels of mercury and cadmium but lead is still present in Leclanché ones [13]. However, only a little more than 15% of Brazilian municipalities present licensed landfills. Since collection of spent batteries is still incipient, most of them are discarded improperly in the environment.

The definite solution to this question is to develop recycling processes for spent batteries. They could be regarded as a secondary source of zinc and manganese [2,3,14,15]. Due to the rising demand and limited natural resources supply, many valuable metals including manganese and zinc have been listed as the strategic metals by many countries [16,17].

The methodologies used to recover valuable metals from spent batteries use preliminary physical methods of separation followed by pyro [18,19] or hydrometallurgical treatments [9,14,20] to recover the valuable metals under various forms [3]. However for both routes there are still challenging questions because of a series of reasons. First of all the minimum admissible purity of the recycled products may be attained only in the absence of some foreign elements in the wastes or in the presence of limited amounts of impurities in the wastes. This raises the stringent problem of avoiding cross contamination when spent batteries of different chemical nature are collected together. As a consequence selective sorting of such wastes by a safe, rapid and not costly method is an imperative requirement. This is so because the set of recycling operations is specific for each type of spent batteries according to their chemical nature. A second aspect that makes recycling of spent batteries a challenging scientific field is the need to enhance the recovery efficiency for each metal by a thorough investigation of the process parameters [4].

Leached zinc and manganese can be separated by several methods such as chemical precipitation [4,18,20,21], liquid–liquid extraction [22] and electrowinning [20]. Metals present in small amounts may influence the purity of final products.

Taking into account the high amounts of manganese found in the electroactive components of spent Zn–MnO₂ dry cells, this material has been regarded as a possible source for direct synthesis of specific manganese compounds [23]. Under this assumption, this material could be investigated as a source for production of potassium manganate (K₂MnO₄) and potassium permanganate (KMnO₄). The existing processes for manufacturing K₂MnO₄ (roasting and liquid phase ones) employ pyrolusite as raw material (>60 wt% MnO₂); the level and type of impurities vary from ore to ore. Preparation of K₂MnO₄ was much investigated in the early XXth century because of the wide use of K₂MnO₄ and BaMnO₄ (a water-insoluble salt) for water purification [24,25]. In short, pyrolusite is dried and ground, mixed with KOH and heated under suitable conditions in the presence of water and O₂ (air). This conversion is very sensitive to experimental conditions (temperature, amount of oxidant and KOH). The fused mass is dissolved in water (producing a dark-green K₂MnO₄ solution) containing KOH (pH 14) so as to avoid decomposition of the MnO₄²⁻ anion and allow its separation from the insoluble matter. Thus, the manganate ion is electrochemically oxidized to permanganate, MnO₄⁻, followed by crystallization of KMnO₄ [26,27].

Potassium manganate is a potentially powerful oxidizing agent both directly and through its disproportionation products; the electrode potentials of manganate (MnO₄²⁻) and permanganate (MnO₄⁻) ions under standard conditions are very high [28]. Potassium permanganate is an environmentally benign and versatile industrial oxidant. It is used for the purification of drinking water (removal of natural organic matter [NOM]), cleaning of swimming

pools, and treatment of industrial wastewater. It converts all organic material into carbon dioxide and water. It reacts over a wide range of pH and requires no additional catalyst. During oxidation potassium permanganate is reduced to manganese dioxide (MnO₂). The dioxide itself can be recycled, and this feature makes the use of potassium permanganate environment friendly [27–29].

This work describes a route for extracting manganese and zinc from spent zinc–manganese dioxide dry cells via fusion of the electroactive components with potassium hydroxide to form K₂MnO₄ and soluble zincates. The manganese content is then separated from the zinc one by precipitation as BaMnO₄. The influence of reaction time, temperature and amount of KOH were investigated. The insoluble matter obtained after treatment of the fused mass with water was characterized and leached elements were recovered by classical precipitation techniques.

2. Experimental

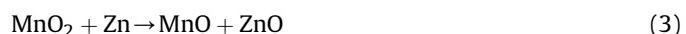
2.1. Samples

Spent AA zinc–MnO₂ dry cells (alkaline and Leclanché) were employed in this work. The AA format is the most current size employed in Brazil. Their expiry date was between January–October 2013. Alkaline and Leclanché dry cells were processed separately. Samples were manually dismantled (using gloves, glasses and dust masks) in order to recover the electroactive components (electrolyte, cathode, anode). The mixed material was ground for 30 min by a ball mill. This mass was dried at 40 °C for 24 h [13]. Other components such as plastic and paper films, ferrous and non-ferrous scraps and carbon rods were identified and separated.

2.2. Pre-oxidation of the dried electroactive components

The dried masses were placed in ceramic crucibles. Pre-oxidation was performed in a furnace at 500 °C for 3 h [7]. The objective was to eliminate carbon (as CO₂) before fusion of the samples with KOH since it reduces manganese in high oxidation states (4+ to 7+) and reacts with KOH producing K₂CO₃, which is not reactive. The roasted mass was cooled down in the furnace and transferred to a dessicator before running the experiments.

Commonly, zinc–MnO₂ dry cells batteries are not fully exhausted, therefore they contain some metallic zinc [21]. This residual zinc and the carbon present in the positive electrode react with Mn(IV)/Mn(III) under heating [18]:



Pre-oxidation was performed under a slow heating rate (3 °C min⁻¹) so as to avoid any violent reaction due to the metallic zinc. Oxygen converts zinc and lead (if present) into ZnO and PbO, respectively.

It is worth commenting on the pre-oxidation of the electroactive components of spent Leclanché dry cells. Ammonium salts (typically, NH₄Cl) are present in their electrolytes. This salt sublimes at ~340 °C (it decomposes into NH₃ and HCl) and is readily soluble in water (~550 g L⁻¹ at 25 °C) [30], giving an acidic solution due to hydrolysis of NH₄⁺ cations [30]. For this reason the gaseous effluent

of the furnace was passed through distilled water at 25 °C when processing electroactive components of spent Leclanché dry cells.

2.3. Fusion process

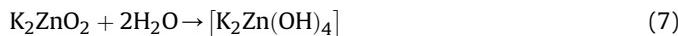
K_2MnO_4 was prepared using the method described in the literature [27,31,32]. Experiments were carried out in 1–10 g scale.

The pre-oxidized sample was mixed with 6 mol L⁻¹ potassium hydroxide (the KOH/sample mass ratio varied from 0.9 to 2.0) in a nickel crucible. The mixture was heated until evaporation of the aqueous phase. Oxidation of manganese was performed in three stages. In the first one, the dried mixture was introduced in a furnace at a given temperature (200–350 °C, 3 °C min⁻¹) for 1–5 h. Air (20 mL min⁻¹) was passed over the mixture with help of a sparging device. It was previously passed through 6 mol L⁻¹ NaOH to eliminate CO₂. The crucible was removed from the furnace and placed over a hot plate (150 °C). 10 mL of water were added. After evaporation the mixture was reintroduced into the furnace at the original temperature (200–350 °C) for 1 h. This cycle was performed two times. Small amounts of water present a positive effect on the conversion of MnO₂ to K_2MnO_4 [24,25,30]. The final roasted mass was cooled down in the furnace and leached with 0.7–10 mol L⁻¹ KOH (30 mL g⁻¹) at 25 °C for 30 min and stirring at 200 rpm. The insoluble matter (a brown solid) was separated from the dark-green liquid phase by filtration (sintered glass filter) under vacuum and washed with 0.1 mol L⁻¹ KOH (3 mL g⁻¹ solid) and water (1 mL g⁻¹ solid). The washed solid was dried at 150 °C for 3 h and weighed. The progress of the fusion was monitored by the amount of the insoluble matter and the amount of manganese converted into manganate ions after each experiment. The experiments were run in triplicate, and errors for each experiment were always below 5%.

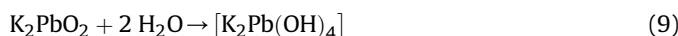
The reactions involving manganese dioxide and potassium hydroxide are very complex due to formation of several intermediate compounds [24,25,31,32], but the overall conversion may be expressed by the following equation:



Zinc oxide is amphoteric and also reacts with KOH. Potassium zincate is soluble in water:



Taking into account the other elements present in spent Zn–MnO₂ dry cells [11,15,16,18], lead(II), silicon, chromium(III) and aluminum(III) oxides also react with KOH forming water-soluble compounds. This aspect is of great importance since Brazilian Leclanché Zn–MnO₂ dry cells still contain lead [7,13].



The aqueous dark-green solution was processed to crystallize potassium manganate (Section 2.4) or to precipitate the manganate anion as barium salt (Section 2.5).

2.4. Crystallization of potassium manganate

A saturated KOH solution (~20 mol L⁻¹) was slowly added to the dark-green solution at 25 °C and 200 rpm. The final KOH concentration was set at 3–17.5 mol L⁻¹. The mixture was cooled in an ice bath. After 10–15 min the formed K_2MnO_4 crystals were filtered through a sintered glass filter under vacuum [33]. They were pressed against the filter using a watch glass so as to drain as much liquid as possible. The solid must not be washed with water or diluted KOH (<0.05 mol L⁻¹) because it dissolves and decomposes K_2MnO_4 . The solid exhibits a violet-brown reflex like KMnO₄ crystals. It was then placed on a porous plate in a dessicator over KOH and dried by evacuation for 2 h. Since K_2MnO_4 is deliquescent, the dried solid was placed in a sealed glass vessel.

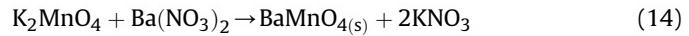
2.5. Conversion of potassium manganate to barium manganate

Although BaMnO₄ is an expensive salt, it finds wide use in organic chemistry as oxidant for conversion of allylic and benzylic alcohols to aldehydes, diols to lactones, thiols to disulfides, aromatic amines to azocompounds, benzylamine to benzaldehyde, hydroquinone to *p*-benzoquinone etc. [29,34]. Conversion of K_2MnO_4 to the barium salt also serves as a gravimetric method for determination of soluble manganese since BaMnO₄ is water-insoluble ($K_{sp} = 2.46 \times 10^{-10}$ [30,35]) and K_2MnO_4 isolated by crystallization (Section 2.4) was not washed to remove water-soluble impurities (particularly KOH).

During precipitation the final pH must be kept above 13 in order to avoid disproportionation of manganate ions:



KOH concentration varied from 0.7 to 10 mol L⁻¹. 0.2 mol L⁻¹ Ba(NO₃)₂ was added under magnetic stirring (200 rpm) at 25 °C. A dark-green solid (BaMnO₄) was obtained:



It was isolated by filtration (sintered glass filter) under vacuum and washed with 0.05 mol L⁻¹ KOH (2 mL g⁻¹ solid) and water (0.5 mL g⁻¹ solid), dried at 110 °C for 1 h and weighed.

2.6. Recovery of soluble zinc

After precipitation of barium manganate 1 mol L⁻¹ K₂SO₄ was added dropwise to the colorless filtrate containing Zn(II) under stirring (200 rpm) at 25 °C in order to precipitate excess Ba²⁺ and lead (if present) as sulfates (BaSO₄, PbSO₄). pH must be always kept above 13 in order not to decompose [Zn(OH)₄]²⁻ ions, thus precipitating Zn(OH)₂.

Zinc was isolated by adding 6 mol L⁻¹ H₂SO₄ under stirring (200 rpm) at 25 °C. Final pH must be in the range 7–8. The white solid was filtered and washed with water (5 mL g⁻¹) to remove K⁺, OH⁻ and SO₄²⁻ ions, dried at 110 °C for 3 h and weighed.

2.7. Crystallization of K₂SO₄

The neutralized solution was slowly evaporated to 1/3 of the initial volume at 60–70 °C (without stirring). After this step the new solution was cooled in an ice bath. A white solid was filtered, washed three times with ethanol (3 mL g⁻¹) and dried at 25 °C.

Fig. 1 presents the overall scheme for processing the leachates.

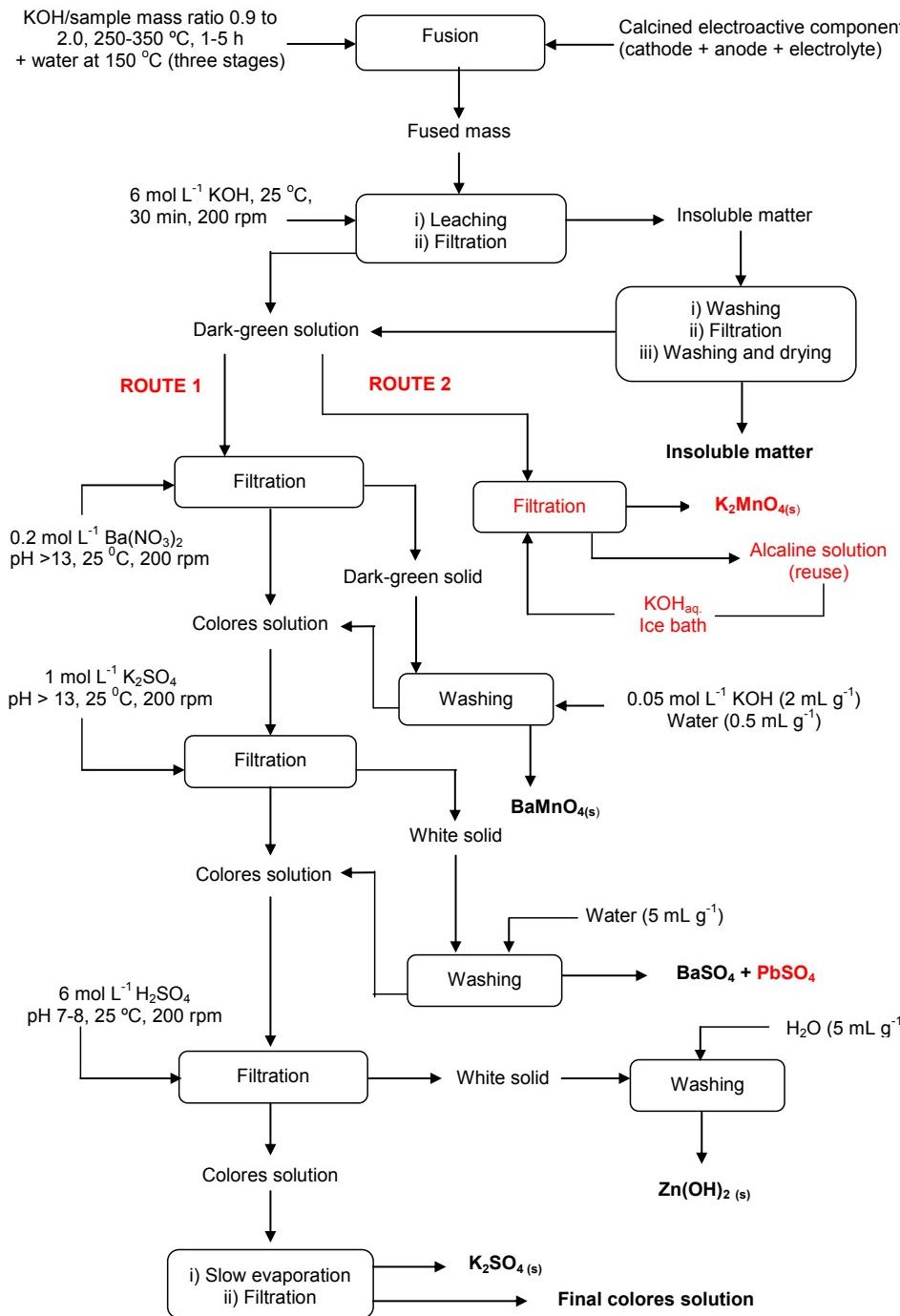


Fig. 1. General scheme for recovery of zinc and manganese from spent zinc–MnO₂ dry cells after fusion with KOH and leaching with water.

2.8. Separation of potassium permanganate from soluble zinc

Although the conversion of K₂MnO₄ to KMnO₄ was not performed in this study (it is a well-established industrial procedure [27,31,32]), it is interesting to know if it is possible to crystallize KMnO₄ from the leachate containing zinc and lead. For this purpose, the calculated amount of KMnO₄ that would be obtained from the electrochemical oxidation of leached K₂MnO₄ was dissolved in the same volume of aqueous KOH (0.7–10 mol L⁻¹) containing the same concentrations of zinc, aluminum and lead in the leachates. The resulting violet solution was then crystallized [27,31,32,36] at ~10 °C.

2.9. Analytical methods

The whole spent battery, the components obtained during sample dismantling and the solids obtained during processing of electroactive components were weighed in an analytical balance (Scientech SA 120). The electroactive components of the batteries, the insoluble matter isolated after leaching with water and the solids obtained during separation procedure were also analyzed by X-ray fluorescence (Shimadzu XRF 800HS). Calibration curves (0.1–1000 mg kg⁻¹) for manganese, zinc, lead, barium, aluminum and potassium were employed for quantitative analyses of these elements. Metal concentrations in the leachates were determined

by atomic absorption spectrometry (Perkin Elmer AAS 3300). The following wavelengths were employed: aluminum, 309.3 nm; barium, 553.6 nm; zinc, 213.9 nm; manganese, 279.5 nm; lead, 283.3 nm; potassium, 766.5 nm. The following detection limits were determined experimentally: 1 mg L⁻¹ (potassium), 0.5 mg L⁻¹ (other elements). The solids were dissolved in water at 25 °C (K₂SO₄), 1 mol L⁻¹ HCl + 10 wt% H₂O₂ at 40 °C (BaMnO₄ and Zn(OH)₂), 1 mol L⁻¹ HNO₃ + 10 wt% H₂O₂ at 50 °C (insoluble matter in water after fusion) or 0.01 mol L⁻¹ EDTA (BaSO₄ and lead sulfates). Alkalinity of the aqueous solutions was determined by potentiometry using an Ag/AgCl reference electrode (Orion 2A13-JG). Crystalline phases in the solid samples were identified by X-ray diffraction analysis (Shimadzu model XRD 6000) by continuous scanning method at 20 mA and 40 kV, using Cu K α as the radiation source.

3. Results and discussion

3.1. Composition of the pre-oxidized electroactive components of the batteries

The average composition of these samples is shown in Table 1. These results agree with our previous data [7,13,18], thus confirming that lead was only found in Brazilian Leclanché cells.

Data on this table also demonstrate that carbon removal increases MnO₂ content to a level that meets the minimum amount normally found in raw materials for industrial production of K₂MnO₄ [31,32,36].

3.2. Effect of the KOH/sample mass ratio

The experiments were accomplished at 250 °C for 3 h (first stage) and 250 °C for 1 h (2nd and 3rd stages). The results are presented in Fig. 2 as a function of the amount of insoluble matter in aqueous KOH after leaching of the fused mass. The lower the insoluble matter the higher the conversion of manganese and zinc to water-soluble forms (Eqs. (5)–(7)).

Taking into account the stoichiometry of reactions (5) and (6) (KOH/MnO₂ mol ratio = 2; KOH/MnO₂ mass ratio = 1.29; KOH/ZnO mol ratio = 2; KOH/ZnO mass ratio = 1.38) and the amounts of these elements in the pre-oxidized electroactive components (Table 1), the theoretical KOH/sample mass ratio is in the range 1.25–1.30.

Table 1

Average composition^a (wt%) of the electroactive components of zinc–MnO₂ dry cells^b after pre-oxidation and of the insoluble matter in water after fusion with KOH (250 °C, 1 h, three stages; KOH/sample mass ratio 1.3) (dry basis).

Element ^a	Electroactive components		Insoluble matter	
	Leclanché	Alkaline	Leclanché	Alkaline
Mn	53.4	66.0	32.0	44.3
Zn	43.5	26.8	60.8	45.4
Si	0.3	0.2	0.6	0.6
Fe	0.9	0.5	1.8	1.5
K	0.7	6.0	4.0	7.4
Na	1.0	0.2	0.2	Not detected
Pb	3×10^{-2}	Not detected	4×10^{-2}	Not detected
Ca	7×10^{-2}	0.1	0.2	0.3
Al	0.1	1×10^{-2}	0.2	2×10^{-2}
Ni	3×10^{-3}	8×10^{-2}	7×10^{-3}	0.2
Cu	7×10^{-3}	7×10^{-2}	2×10^{-2}	0.2
Cr	4×10^{-3}	1×10^{-2}	9×10^{-3}	2×10^{-2}
Ti	1×10^{-2}	3×10^{-2}	2×10^{-2}	0.1

^a Hg and Cd are present in amounts below 10 µg kg⁻¹ in Brazilian zinc–MnO₂ dry cells [7,13].

^b C comprises 27.0 and 35.5 wt% of the original electroactive components of Leclanché and alkaline cells, respectively [7,13,18].

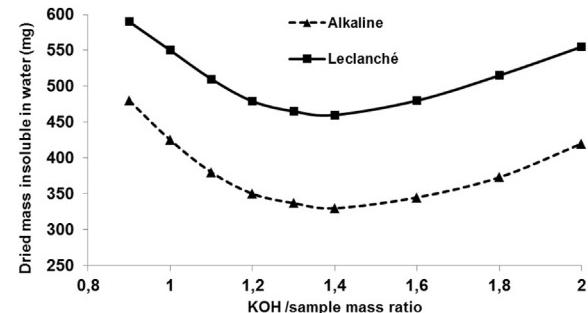


Fig. 2. Effect of the KOH/sample mass ratio on fusion of the electroactive components of spent zinc–MnO₂ dry cells at 250 °C for 3 h (1st stage) and 250 °C for 1 h (2nd and 3rd stages). Base: 1 g sample.

The amount of insoluble matter after fusion below this range was very high since there was not enough reactant to convert all the reactive elements into water-soluble compounds. The optimum KOH/sample mass ratio was somewhat higher than the theoretical values, but the optimum zone is in a very narrow range (1.3–1.4). Ratios above 1.4 presented a negative effect on the course of reaction. K₂MnO₄ tends to be decomposed under high KOH excess in a wide temperature range (200–400 °C), forming a water-insoluble solid (such as xK₂MnO₄·yK₂MnO₃·zK₂O) [24,25,37]. Solids like this explain the higher potassium amount found in the insoluble matter (Table 1). For this reason, addition of water between fusion stages prevents or minimizes formation of such insoluble solids containing manganese [24–26,29,37].

It must be emphasized that the best KOH/sample mass ratio depends on the fraction of the sample that reacts with the base (Mn, Zn, Pb, Al, Si). As the amount of non-reactive species in a given sample increases the KOH/sample mass ratio decreases as less reactant is necessary to treat the sample [25–27].

3.3. Effect of temperature and time

In this study the first stage of the fusion was conducted in the range of 200–350 °C, using a KOH/sample mass ratio equal to 1.4. The results are presented in Fig. 3.

The mass of insoluble matter in water slowly decreased as fusion temperature increased from 200 to 240 °C. Temperatures in the range 240–250 °C fall in the best zone to convert MnO₂ into K₂MnO₄ [25,27,31,32]. Temperatures above 250 °C presented a negative effect on manganese conversion, especially at high KOH/sample mass ratios. This is ascribed to the formation of

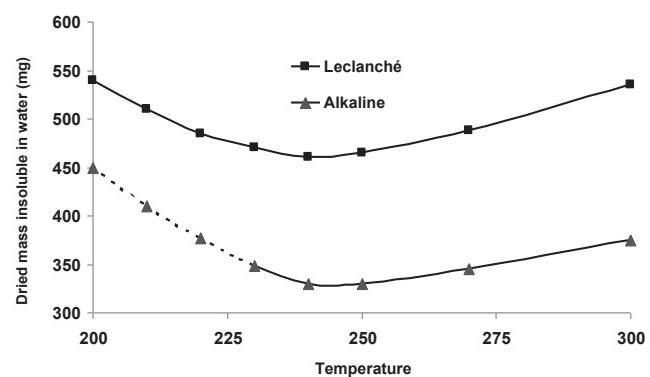


Fig. 3. Effect of temperature and time on fusion of the pre-oxidized electroactive components of spent zinc–MnO₂ dry cells with KOH (KOH/sample mass ratio = 1.4, 1 g sample).

potassium–manganese oxides ($x\text{K}_2\text{MnO}_4 \cdot y\text{K}_2\text{MnO}_3 \cdot z\text{K}_2\text{O}$) [25,26,37] under these circumstances, as already discussed in Section 3.2.

Long times (>1 h) in the first stage did not present any influence of fusion behavior. Leaching of the fused mass with KOH was not sensitive to its concentration range tested (0.7–10 mol L⁻¹). The insoluble matter remained constant whatever the concentration of the strong base used for leaching.

As a general conclusion fusion of electroactive components of spent Zn–MnO₂ dry cells with KOH must be conducted under controlled experimental conditions in order to avoid undesirable side reactions. Fusion between 240 °C and 250 °C for 1 h under a KOH/sample ratio 1.3–1.4 is the choice because of the i) lower energy consumption, ii) lower consumption of reactants and iii) maximum yield of soluble manganese. The best temperature and KOH/sample mass ratio found in this study are comparable to data for MnO₂ using the method described in this work [27,31,32]. This suggest that the electroactive components of spent Zn–MnO₂ dry cells behave similarly to pyrolusite and related MnO₂ concentrates that are usually employed as raw material for K₂MnO₄ industrial synthesis. An essential pre-requisite is to remove carbon prior to fusion as already discussed in Section 3.1.

The chemical composition of the insoluble matter in water after fusion (XRF data) is given in Table 1. Manganese and zinc are by far the most abundant elements. Taking into account the average mass (460 mg g⁻¹ dried mass – Leclanché batteries, 330 mg g⁻¹ dried mass – alkaline ones), titanium, calcium, iron, nickel, copper, aluminum, chromium and silicon were not leached to a significant extent, despite the three latters react with KOH forming water-soluble compounds (reactions (10)–(12)) [30]. The formation of mixed oxides (not detected by XRD due to their low amounts) or the mild experimental conditions [36–38] can account for these results.

On the other hand, potassium is more abundant in the insoluble matter even in the case of alkaline batteries, since KOH is its electrolyte [18]. This is explained by the insoluble manganese–potassium compounds as discussed earlier. The higher the manganese content, the higher the amount of potassium.

The Mn/Zn mass ratio in the insoluble matter is about 0.97 (alkaline cells) and 0.53 (Leclanché ones). These ratios are much lower than those found in the original dried masses (Table 1: 2.46 and 1.22 for alkaline and Leclanché cells, respectively). This result indicates that zinc was less leached by aqueous KOH than manganese. Based on data of Table 1, under the best experimental conditions, 72 wt% (Leclanché) and 78 wt% (alkaline) of manganese and 30 wt% (Leclanché) and 44 wt% (alkaline) of zinc were leached. The results for manganese are 15–20% lower than the yields reported (85–95 wt%) when pyrolusite or other related materials are employed [27,31,32,36]. Nevertheless this result should be regarded as encouraging since the amount and identity of the metal impurities (particularly zinc) in the pre-oxidized spent electroactive components of spent Zn–MnO₂ dry cells are quite different from those normally found in the current materials used for industrial synthesis of K₂MnO₄ [34,37].

X-ray diffraction data of the insoluble matter after fusion at 250 °C for 1 h (three stages) are shown in Fig. 4. A distinct behavior was found for alkaline and Leclanché cells. The peaks all correspond to manganese compounds (K₂MnO₃, MnO₂) for alkaline cells, whereas mixed Zn–Mn^{3+/4+} oxides (hetaerolite) were observed for Leclanché ones. These results correlated to the chemical data (Table 1): the higher amounts of potassium and manganese in the alkaline samples, and the higher amounts of zinc in the Leclanché ones. As a conclusion, it appears that zinc and potassium may affect conversion of MnO₂ to K₂MnO₄. High amounts of zinc tend to react with manganese oxides forming water-insoluble oxides like those

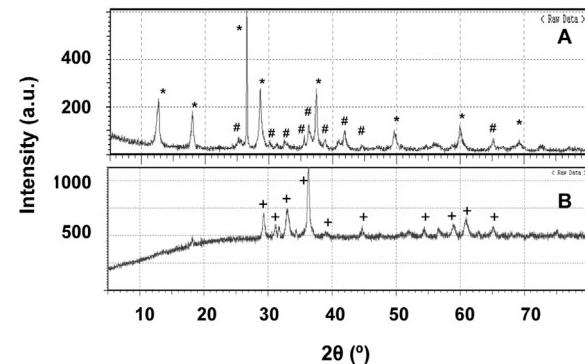


Fig. 4. X-ray diffractogram of the insoluble residue in water after fusion of the pre-oxidized electroactive components of spent alkaline cells (A) or spent Leclanché ones (B) with KOH at 250 °C for 1 h (three stages; KOH/sample mass ratio = 1.4). The peaks marked * represent MnO₂, those marked # represent K₂MnO₃ and those marked + represent ZnMn₂₋₃O₄ (hetaerolite).

detected by XRD. Potassium and manganese can form mixed insoluble compounds [25,26,31] according to the fusion conditions.

After solubilization of the insoluble matter (Section 2.6) a colorless solution containing Mn²⁺ ions [30] was obtained, thus confirming that insoluble manganese is in 3+ and 4+ oxidation states.

3.4. Metals concentration in the leachates

Table 2 presents the concentration of leached species. Besides zinc, manganese, lead (only for Leclanché batteries) and aluminum, sodium and potassium were also detected. This latter comes from both the fused mass and the aqueous KOH used to dissolve it. As expected from data of the insoluble matter (Table 1), the other elements present in the electroactive components of spent Zn–MnO₂ dry cells were not found. In practice only lead is an interfering element in the leachate. The concentration of manganese and zinc in the leachates corresponds to the amount leached according to data presented in Table 1, thus confirming that alkaline Zn–MnO₂ dry cells gave better results than Leclanché ones for both elements.

3.5. Recovery of manganese as potassium manganate

According to data on Table 3, the best KOH concentration corresponds to saturation (17.5 mol L⁻¹ at 0 °C): over 90 wt% of leached manganese was crystallized as K₂MnO₄. KOH decreases its solubility due to the common ion effect [30]. The yield was higher for alkaline Zn–MnO₂ dry cells due to the higher concentration of the salt (Table 2).

No zinc and lead were found in crystallized K₂MnO₄. This is basically due to their low content in the leachates. However, the solid is not pure K₂MnO₄. The higher the concentration of KOH the higher the amount of potassium in the crystallized solid. A small amount of the solid was dissolved in 2 mol L⁻¹ NaOH at 25 °C. No

Table 2
Metallic ions in the leachates.

Battery type	Mn (g L ⁻¹)	Zn (g L ⁻¹)	Pb (mg L ⁻¹)	Al (mg L ⁻¹)
Alkaline	7.46 (16.14 g L ⁻¹ as MnO ₄ ²⁻)	1.71 (3.49 g L ⁻¹ as [Zn(OH) ₄] ²⁻)	Absent	0.15 (0.52 mg L ⁻¹ as [Al(OH) ₄] ⁻)
Leclanché	5.42 (11.72 g L ⁻¹ as MnO ₄ ²⁻)	1.89 (3.85 g L ⁻¹ as [Zn(OH) ₄] ²⁻)	1.30 (1.73 mg L ⁻¹ as [Pb(OH) ₄] ²⁻)	0.10 (0.35 mg L ⁻¹ as [Al(OH) ₄] ⁻)

Table 3Average metals composition of crystallized K_2MnO_4 .

KOH (mol L ⁻¹)	Yield (wt%)		Average metal content (wt%)				
	Alkaline	Leclanché	Mn ^a	Zn	Pb	K ^a	Al
5	0	0	—	—	—	—	—
8	5	—	27.7	<0.1	<0.1	39.9	<0.1
10	55	40	27.4	<0.1	<0.1	40.2	<0.1
15	85	79	26.5	<0.1	<0.1	41.1	<0.1
17.5	97	92	25.1	<0.1	<0.1	42.8	<0.1

^a Theoretical values for K_2MnO_4 : 39.6 wt% K and 27.9 wt% Mn.

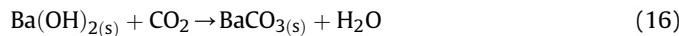
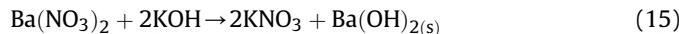
precipitate (MnO_2) was found. It is likely that some KOH is present in crystallized K_2MnO_4 .

Crystallization of K_2MnO_4 requires a highly concentrated KOH solution. Although this procedure is technically feasible in laboratory scale, this is not the normal industrial practice. It is the intermediate for preparation of $KMnO_4$. The fused mass is dissolved in aqueous KOH and MnO_4^{2-} ions are converted via electrochemical routes to MnO_4^- [26,27].

As in the industrial preparation of $KMnO_4$ [32,36,39], the alkaline liquor can be recycled [33]. However the number of cycles is limited by the concentration of zinc. If this element begins to co-crystallize with K_2MnO_4 , the alkaline solution must be treated to recover zinc (Sections 2.6 and 3.8) and potassium sulfate (Sections 2.7 and 3.9).

3.6. Recovery of manganese as barium manganate

Table 4 presents the chemical analysis of barium manganate precipitated at various KOH concentrations. The purity of this solid is very dependent on the amount of KOH used to leach the fused mass: the higher the concentration the higher the amount of barium in the solid, surpassing the theoretical amount in the manganate salt (60 wt%). XRD data (Fig. 5) show that the other barium compound present in this solid is barium carbonate, which comes from precipitation of $Ba(OH)_2$ followed by reaction with CO_2 :



Since barium hydroxide is only moderately soluble in water ($K_{sp} = 8 \times 10^{-3}$ [30]), the increase of KOH concentration (i.e., OH^- ions) tends to favor co-precipitation of $Ba(OH)_2$ together with $BaMnO_4$. Therefore, the amount of KOH used to dissolve the fused mass must be minimal to overcome this difficulty but must ensure leaching of K_2MnO_4 without risk of its disproportionation (reaction (13)). pH must be kept above 13 for such [25–27,30,39]. At the same time pH of the leachate must ensure solubilization of reacted zinc (reactions (6) and (7)), which is also above 13 [30]. The minimum

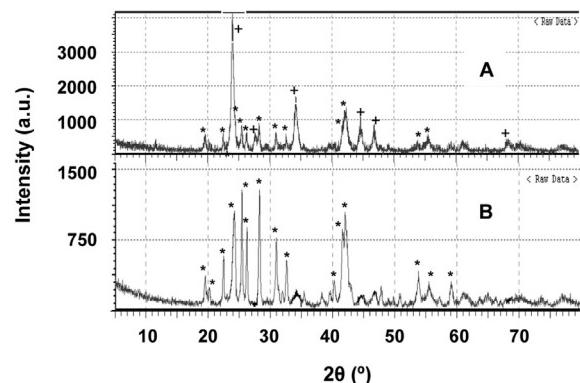


Fig. 5. Typical X-ray diffractogram of the solid recovered after precipitation of manganate ions with aqueous $Ba(NO_3)_2$ in 6 mol L⁻¹ KOH (A) or 1 mol L⁻¹ KOH (B). The peaks marked * represent $BaMnO_4$, and those marked + represent $BaCO_3$.

KOH concentration to satisfy simultaneously all these criteria is 0.7 mol L⁻¹. In practice it is advisable to employ a somewhat higher concentration (~1 mol L⁻¹, pH 14) in order to avoid reduction of pH by atmospheric CO_2 and acidic impurities present in the vessel. Although $Ba(OH)_2$ is leachable by water, the amount of water used for washing crude $BaMnO_4$ should be the as least as possible (~0.5 mL g⁻¹ solid) in order to avoid its disproportionation (reaction (13)).

$BaMnO_4$ isolated in 0.7–1 mol L⁻¹ KOH is a non hygroscopic dark-green solid (in contrast to K_2MnO_4), stable to air. More than 99.8 wt% of leached manganese (**Table 2**) was precipitated, this is in agreement with its very low K_{sp} [35]; the filtrate is colorless and manganese was not detected. XRD data of this solid (**Fig. 5**) show only peaks due to $BaMnO_4$, in contrast to the profile shown when this salt was isolated in 6 mol L⁻¹ KOH. It is remarkable that lead and zinc are absent in this solid, as they remained soluble as hydroxycomplexes [30] at pH ~14.

3.7. Separation of potassium permanganate from soluble zinc and lead

According to data on **Table 2**, $[KMnO_4]$ was in the range 0.100 mol L⁻¹ (Leclanché dry cells) and 0.136 mol L⁻¹ (alkaline dry cells). As expected, $KMnO_4$ crystallized as prismatic purplish-black glistening crystals [36]. The yield of crystals increased as KOH concentration increased (**Table 5**) and was higher for alkaline cells due to the higher concentration of the salt. At 10 °C the solubility of $KMnO_4$ in pure water is 43 g L⁻¹ ($K_{sp} = 7.3 \times 10^{-2}$) [36]. KOH decreases solubility of the salt due to the common ion effect [30].

No zinc and lead were found in crystallized $KMnO_4$. Its purity is very high (>99.5 wt%). The absence of zinc and lead is basically due to their low content in the leachates. This result reinforces the

Table 4Average metals composition of $BaMnO_4$ precipitated at various KOH concentrations.

KOH (mol L ⁻¹)	Metals (wt%) ^a			Average composition (wt%)	
	Ba (as BaO)	Mn (as MnO)	K (as K_2O)	$BaMnO_4$	$BaCO_3$
0.7	60.0	27.8	Negligible	>99.5	<0.5
1.0	60.2	27.7	Negligible	99.5	0.5
3.0	63.1	22.6	0.1	81.5	18.5
5.0	65.5	18.9	0.2	68.1	31.9
10.0	75.0	4.2	0.2	15.0	85.0

^a Al and Pb were not detected in the solids. Theoretical values for $BaMnO_4$: 59.8 wt% BaO and 27.7 wt% MnO.

Table 5Average metals composition of crystallized $KMnO_4$.

KOH (mol L ⁻¹)	Yield (wt%)		Metal content (wt%) ^b				
	Alkaline	Leclanché	Mn ^a	Zn	Pb	K ^a	Al
0.7	30	6	34.7	<0.1	<0.1	24.8	<0.1
1	50	34	34.9	<0.1	<0.1	24.9	<0.1
2	72	65	34.7	<0.1	<0.1	24.7	<0.1
3	80	73	34.7	<0.1	<0.1	24.8	<0.1
5	87	82	34.8	<0.1	<0.1	24.8	<0.1
10	94	89	34.7	<0.1	<0.1	24.9	<0.1

^a Theoretical values for $KMnO_4$: 24.7 wt% K and 34.8 wt% Mn.

^b Data for simulated leachate of alkaline cells.

Table 6

Average metals composition of the solid containing lead and barium and the final zinc product (ZnO) (wt%).^a

Metal	Solid containing lead and barium		Solid containing zinc	
	Leclanché	Alkaline	Leclanché	Alkaline
Mn	<0.1	<0.1	<0.1	<0.1
Zn	0.1	0.1	80.0	80.2
Pb	90.9	Absent	<0.1	Absent
K	3.6	2.9	0.1	<0.1
Al	<0.1	<0.1	<0.1	<0.1
Ba	5.4	97.0	0.1	0.1

^a Theoretical value for ZnO : 80.3 wt% K. Except for Ba and K, the other elements are below the detection limit.

possibility of use of the electroactive components of spent $Zn-MnO_2$ dry cells as an alternative raw material for preparation of $KMnO_4$. After crystallization, the alkaline liquor can be recycled [32,36,39]. However as in the case of K_2MnO_4 , the number of cycles will be limited by the concentration of zinc.

3.8. Recovery of leached zinc

After precipitation of $BaMnO_4$, the basic pre-requisite to obtain a pure zinc precipitate is to remove excess barium and lead, otherwise the three elements tend to precipitate together. As shown in Fig. 1 the strategy was to precipitate lead and barium sulfates. Lead(II) sulfate ($PbSO_4 - K_{sp} = 2.5 \times 10^{-8}$ [30]) is insoluble enough to displace the element from $[Pb(OH)_4]^{2-}$, which is not very stable [31,40]. Data on Table 6 show the absence of zinc (and also manganese) in this precipitate. Lead (Leclanché dry cells) or barium (alkaline ones) is largely the major element of this solid, but its mass is very small (~1.5 mg g⁻¹ dried mass). The white precipitate containing zinc is very pure (99.6 wt% as ZnO), only tiny amounts of barium were found. This solid contains 99.5 wt% of the element leached after fusion (Table 2), and corresponds to ~30 wt% and ~43 wt% of the element present in the pre-oxidized electroactive components of spent Leclanché and alkaline $Zn-MnO_2$ dry cells, in agreement with data for the insoluble matter in KOH after fusion (Table 1 and Section 3.3).

After crystallization of K_2MnO_4 (Section 3.5), the procedure described above can be applied to recover zinc from the alkaline solution. Precipitation of insoluble sulfates is only applicable when lead is present (Leclanché dry cells). The white precipitate containing zinc is very pure (>99.5 wt% as ZnO), containing tiny amounts of potassium. This solid contains 99.5 wt% of the element. Since the initial KOH concentration is very high (17.5 mol L⁻¹) the amount of potassium sulfate formed upon neutralization can surpass the solubility of this salt in water (120 g L⁻¹ at 25 °C, 230 g L⁻¹ at 90 °C [30]). The best technique to precipitate zinc without the interference of K_2SO_4 is to add diluted H_2SO_4 (3 mol L⁻¹) at 90–100 °C.

3.9. Analysis of the crystallized solid after evaporation of the neutralized effluent

Its typical diffractogram (Fig. 6) shows a crystalline material and the peaks correspond to K_2SO_4 [26]. Potassium comprises 44.7 wt% of the solid (44.83 wt% for K_2SO_4). Lead, zinc, barium and aluminum (Table 1) were not detected. The use of this salt is critically dependant on the amounts of toxic elements (Ba, Pb) found in the treated samples or added during precipitation of $BaMnO_4$. The use of K_2SO_4 to precipitate soluble barium and lead avoided introduction of foreign cations (such as Na^+). The (slow) evaporation of the

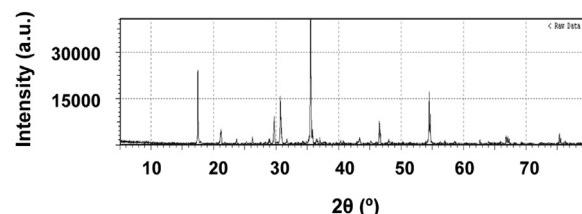


Fig. 6. Typical X-ray diffractogram of the solid recovered after slow evaporation of the final neutralized effluent. The peaks represent K_2SO_4 .

final neutralized solution was limited to 1/3 of the initial volume in order to avoid the presence of foreign elements such as sodium and aluminum.

The amount of recovered K_2SO_4 depends on the manganese compound recovered. In the case of $BaMnO_4$, taking into account the average mass of K_2SO_4 isolated after crystallization (5.7 g g⁻¹ dried mass after fusion (three stages) at 250 °C for 1 h, KOH/sample mass ratio = 1.4) and the amounts of K_2SO_4 , KOH and H_2SO_4 employed (Fig. 1), about 75 wt% of potassium was recovered in this solid. This result agrees with our previous data for processing spent batteries and catalysts via acid fusion [18,41]. For K_2MnO_4 , recovery reached ~95 wt% because of the higher KOH concentration employed to crystallize this salt.

Like in the hydrometallurgical routes reported in the literature for spent zinc– MnO_2 dry batteries, various chemical are employed in the process described in this work, one of which is heavily consumed (KOH), followed by H_2SO_4 , K_2SO_4 and $Ba(NO_3)_2$. This is unavoidable because spent batteries are multi-component wastes. However, most KOH and H_2SO_4 can be recovered as K_2SO_4 . Since its purity is very high, this salt can be sold as raw material, thus avoiding landfilling costs [20].

3.10. Final wastes management

The colorless final effluent essentially contains potassium sulfate (and potassium nitrate if $BaMnO_4$ is isolated). Except for potassium and sodium, metals concentration are below the detection limits of the analytical methods used in this work. This is the only final liquid waste and it meets the requirements for disposal according to the Directory 430 from the National Brazilian Environmental Council [42]. About 20 mL of final neutralized waste were generated per g of fused mass, although the volume of water employed to dissolve the fused mass was 30 mL g⁻¹ (Section 2.3). This is due to evaporation for recovery of K_2SO_4 . For this reason final aqueous wastes were generated in lower amounts than in ordinary hydrometallurgical routes [4,9,14–22] for processing spent $Zn-MnO_2$ dry cells.

The insoluble matter in the leachant (aqueous KOH) (Section 3.3) can be either recycled in the route for K_2MnO_4 synthesis [36] or sent to co-processing according to the Directory 264 from the National Brazilian Environmental Council [43].

Aqueous NH_4Cl (pre-oxidation of electroactive components of Leclanché dry cells) cannot be discarded because of its high amount of NH_4^+ ions [43]. However, when the solution reaches saturation (~550 g L⁻¹ at 25 °C [30]), it is possible to heat it to recover the salt as a by-product.

3.11. Rough economic analysis

No detailed study on economics was performed, but it is important to highlight that we employed the usual steps for preparation of K_2MnO_4 from manganese ores or other sources [26,27,31,32,36]. However, there are two relevant differences

between our source and the common manganese raw materials: the presence of carbon and zinc. Pre-oxidation (carbon removal) increases energy consumption and the presence of zinc requires additional separation steps, thus increasing water and chemicals consumption. This metal also tends to reduce the possible number of reuse cycles of the concentrated KOH_{aq.} after crystallization of KMnO₄ and K₂MnO₄ [32,33,36,39].

Some insight can be obtained based on the market value of the reactants and products. The average prices (in the same purity grade) in Brazil are: barium nitrate (99 wt%), US\$ 300 kg⁻¹; zinc oxide (99.5 wt%), US\$ 90 kg⁻¹; potassium sulfate (>95.5 wt%), US\$ 80 kg⁻¹; potassium hydroxide (>85 wt%), US\$ 60 kg⁻¹; sulfuric acid (98 wt%), US\$ 2 L⁻¹; water, US\$ 5 m⁻³; energy, US\$ 0.25 kW h⁻¹; potassium permanganate (>99 wt%) US\$ 400 kg⁻¹; barium manganate (>98 wt%), US\$ 800 kg⁻¹. Table 7 lists the main costs and the market value of the products obtained in this work (base: 1 kg K₂MnO₄).

Barium manganate is a high-value product, but its market is limited. Although K₂SO₄ is a by-product, the amount produced is considerable. The purity grade of this salt has a markedly influence on its price. The purity grade of K₂SO₄ (Section 3.9) is comparable to the one used as fertilizer [36,38]. The main feature is the absence of chloride ions. The contribution of zinc to the revenue is lower because of its lower yield and its lower market value (ZnO) as compared to manganese.

The revenue from K₂SO₄ and zinc must at least compensate the additional energy, water and chemicals consumption due to carbon and zinc. At present, it is likely that the revenue will partially come from money (price surcharge) that consumers will pay for recycling batteries [20].

4. Conclusions

72–78 wt% of manganese and 30–44 wt% of zinc present in spent zinc–MnO₂ dry cells were leached with aqueous KOH after fusion of their electroactive components with potassium hydroxide under the best optimal conditions (KOH/sample ratio 1.4, 250 °C, 1 h, three stages). Results for manganese are 15–20% lower than the

Table 7
Rough economic analysis of the process described in this work.

Item	Alkaline Zn–MnO ₂ dry cells	Leclanché Zn–MnO ₂ dry cells
Pre-oxidized electroactive components	1.9 kg	2.6 kg
KOH (KOH/sample mass ratio 1.4:1)	2.7 kg (US\$ 162)	3.6 kg (US\$ 216)
Estimated energy consumption	40 kW h ⁻¹ (US\$ 10)	40 kW h ⁻¹ (US\$ 10)
Water	138 L (US\$ 0.70)	186 L (US\$ 1)
KOH (KOH 1 mol L ⁻¹ , 30 mL g ⁻¹ fused mass)	7.33 kg (US\$ 465)	10.42 kg (US\$ 625)
Total (for 1 kg K₂MnO₄)	US\$ 637.70	US\$ 852
Ba(NO ₃) ₂	1.33 kg (US\$ 400)	1.33 kg (US\$ 400)
Water (Ba(NO ₃) ₂ 0.2 mol L ⁻¹)	25 L (US\$ 0.10)	25 L (US\$ 0.10)
KOH (KOH 1 mol L ⁻¹)	1.4 kg (US\$ 84)	1.4 kg (US\$ 84)
Total (for 1.3 kg BaMnO₄)	US\$ 484.10	US\$ 484.10
Conc. H ₂ SO ₄	3 L (US\$ 6)	3 L (US\$ 6)
Water (H ₂ SO ₄ 6 mol L ⁻¹)	24 L (US\$ 0.10)	24 L (US\$ 0.10)
Total for precipitating Zn as Zn(OH)₂	US\$ 6.10	US\$ 6.10
Estimated energy consumption	12 kW h ⁻¹ (US\$ 3)	12 kW h ⁻¹ (US\$ 3)
Total for K₂SO₄ crystallization	US\$ 3	US\$ 3
Total cost reactants, energy and water	US\$ 1130.90	US\$ 1345.20
BaMnO ₄	1.3 kg (US\$ 1040)	1.3 kg (US\$ 1040)
ZnO	0.47 kg (US\$ 42.50)	0.58 kg (US\$ 53)
K ₂ SO ₄	10.83 kg (US\$ 866)	15.4 kg (US\$ 1232)
Total value products	US\$ 1948.50	US\$ 2325

yields reported using pyrolusite (MnO₂) or other manganese raw materials described in the literature. Carbon must be eliminated prior to fusion. Lead was only the significant interfering element found in the leachates. Zinc and potassium can act as a sink for manganese, forming water-insoluble compounds, thus reducing the yield of K₂MnO₄.

Since most metal impurities remained in the insoluble matter after leaching the fused mass with water, processing of the leachate was relatively simple. It was possible to separate manganese from zinc via crystallization of K₂MnO₄ under high KOH concentration or selective precipitation of BaMnO₄. A careful pH control (above 13) and KOH concentration (0.7–1 mol L⁻¹) are necessary to obtain this salt with good purity. Zinc recovery was fairly low but was isolated with good purity; a previous barium and lead removal as sulfate may be necessary. The amount of zinc and lead in the (alkaline) leachate did not interfere in the crystallization of KMnO₄ if K₂MnO₄ is electrochemically oxidized. K₂SO₄ was recovered as high purity grade by-product, thus reducing the amount of final aqueous wastes.

This work is an exploratory study to qualify spent batteries an alternative raw material for direct production of K₂MnO₄. Taking into account the encouraging results, it is worth performing further studies on the influence of the experimental parameters to improve conversion of MnO₂ to K₂MnO₄ in the presence of zinc and other elements in spent batteries, thus also reducing the amount of insoluble matter in aqueous KOH after fusion and increasing the revenue of the developed process.

Acknowledgments

Carolina. L. Quintanilha, Renan A. Rocha and Thayná V. Lanxin acknowledge PIBIC/CNPq-UFRJ for a fellowship. We are grateful to CNPq for financial support.

References

- [1] S. Karnchanawong, P. Limpiteeprakan, Waste Manag. 29 (2009) 550–558.
- [2] M.V. Gallegos, L.R. Falco, M.A. Peluso, J.E. Sambeth, H.J. Thomas, Waste Manag. 33 (2013) 1483–1490.
- [3] G. Belardi, F. Medici, L. Piga, J. Power Sources 248 (2014) 1290–1298.
- [4] T. Buzatu, G. Popescu, I. Birloaga, S. Saceanu, Waste Manag. 33 (2013) 699–705.
- [5] M.F. Almeida, S.M. Xará, J.N. Delgado, C.A. Costa, Waste Manag. 29 (2009) 342–349.
- [6] S.M. Xará, J.N. Delgado, M.F. Almeida, C.A. Costa, Waste Manag. 29 (2009) 2121–2131.
- [7] S.C. Câmara, J.C. Afonso, L.I.D. Silva, N.N. Domingues, A. Alcover Neto, Quím. Nova 35 (2012) 82–90.
- [8] D. Komilis, D. Bandi, G. Kakaronis, G. Zouppouris, Sci. Total Environ. 409 (2011) 2555–2566.
- [9] E. Sayilgan, T. Kukrer, F. Ferella, A. Akcil, F. Veglio, M. Kitis, Hydrometallurgy 97 (2009) 73–79.
- [10] M.P.S. Krekeler, H.A. Barrett, R. Davis, C. Burnette, T. Doran, A. Ferraro, A. Meyer, J. Power Sources 203 (2012) 222–226.
- [11] S.M. Shin, G. Senanayake, J.S. Sohn, J.G. Kang, D.Y. Yang, T.H. Kim, Hydrometallurgy 96 (2009) 349–353.
- [12] Directory No 401 from the National Brazilian Environmental Council, Federal Official Journal, November 5, 2008, <http://www.mma.gov.br/port/conama> (accessed 12.12).
- [13] B.O. Silva, S.C. Câmara, J.C. Afonso, R. Neumann, A. Alcover Neto, Quím. Nova 34 (2011) 812–818.
- [14] T.H. Kim, G. Senanayake, J.G. Kang, J.S. Sohn, K.I. Rhee, S.W. Lee, S.M. Shin, Hydrometallurgy 96 (2009) 154–158.
- [15] A.A. Baba, A.F. Adekola, R.B. Bale, J. Hazard. Mater. 171 (2009) 838–844.
- [16] E. Sayilgan, T. Kukrer, G. Civalekoglu, F. Ferella, A. Akcil, F. Veglio, M. Kitis, Hydrometallurgy 97 (2009) 158–166.
- [17] B. Xin, W. Jiang, H. Aslam, K. Zhang, C. Liu, R. Wang, Y. Wang, Bioresour. Technol. 106 (2012) 147–153.
- [18] C.L. Quintanilha, J.C. Afonso, C.A. Vianna, V. Gante, J.L. Mantovano, J. Power Sources 248 (2014) 596–603.
- [19] R. Rácz, P. Ilea, Hydrometallurgy 139 (2013) 116–123.
- [20] F. Ferella, I. Michelis, F. Veglio, J. Power Sources 183 (2008) 805–811.
- [21] L. Ma, Z. Nie, X. Xi, X. Li, Sep. Purif. Technol. 108 (2013) 124–132.
- [22] Y.A. El-Nadi, J.A. Daoud, H.F. Aly, J. Hazard. Mater. 143 (2007) 328–334.

- [23] P. Hu, D. Pan, S. Zhang, J. Tian, A.A. Volinsky, *J. Alloys Compd.* 509 (2011) 3991–3994.
- [24] C.E. Ruby, *J. Am. Chem. Soc.* 43 (1921) 294–301.
- [25] H.I. Schlesinger, V.T. Jackson, E.E. Cordrey, *Indus. Eng. Chem.* 15 (1923) 53–57.
- [26] D.M.O.G. Garcia, Patent application US 5 011 672, 1991.
- [27] K. Subramanian, K.G. Gomathi, K. Asokan, *Ind. Eng. Chem. Res.* 47 (2008) 8526–8532.
- [28] F. Zhao, X. Li, N. Graham, *Sep. Purif. Technol.* 91 (2012) 52–58.
- [29] N. Singh, D.G. Lee, *Org. Process Res. Dev.* 5 (2001) 599–693.
- [30] J. Lurie, *Handbook of Analytical Chemistry*, third ed., Mir, Moscow, 1978 (Chapters 3, 6 and 10).
- [31] R.H. Reidies, M.B. Carus, Patent application US 2 940 823, 1960.
- [32] D. Pletcher, F.C. Walsh, *Other Inorganic Electrolytic Process in Industrial Electrochemistry*, Chapman & Hall, London, 1990, p. 145.
- [33] W.G. Palmer, *Experimental Inorganic Chemistry*, The University Press, Cambridge, 1970, pp. 485–491.
- [34] G. Procter, S.V. Ley, G.H. Castle, in: L. Paquette (Ed.), *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons, New York, 2004, <http://dx.doi.org/10.1002/047084289X.rb003>.
- [35] H.I. Schlesinger, H.B. Siems, *J. Am. Chem. Soc.* 16 (1924) 1965–1978.
- [36] Kirk-Othmer Encyclopedia of Chemical Technology, fifth ed., Wiley, Ney York, 2007 (Volumes 4 and 22).
- [37] C.E. Day, *J. Am. Chem. Soc.* 42 (1920) 294–301.
- [38] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, fifth ed., John Wiley & Sons, New York, 1988 (Chapter 9).
- [39] J.J. D'Ambrisi, Patent application US 4 911 802, 1990.
- [40] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, second ed., Elsevier Butterworth-Heinemann, London, 2010 (Chapter 10).
- [41] S.G. Batista Jr., J.C. Afonso, J. Hazard. Mater. 184 (2010) 717–723.
- [42] Directory No 430 from the National Brazilian Environmental Council, Federal Official Journal, May 16, 2001, <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646> (accessed 03.14).
- [43] Directory No 264 from the National Brazilian Environmental Council, Federal Official Journal, March 20, 2000, <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=262> (accessed 03.14).